B1

(19) Japanese Patent Office (JP)

(11) Unexamined Patent Application No:

11-246901

(12) Unexamined Patent Gazette (A)

(43) Date of Publication: 14 September 1999

(51) Int. Cl.[6]	Class. Symbols	FI	
B 22 F 9/24		B 22 F 9/24	Z
// G 11 B 5/85		// G 11 B 5/85	A

Request for Examination: Not yet submitted Number of Claims: 21 Total of 8 pages [in original]

(21) Application No.: 10-93830

(22) Date of Filing: 2 March 1998

Application subject to the provisions of Article 30(1) of the Patent Law. Presented in written form at the "30th Autumn Convention of the Society of Chemical Engineers, Japan" held by the Society of Chemical Engineers, Japan on 9 August to 10 September 1997

(71) Applicant: 000005119
Hitachi Zosen Corporation
7-89 Minami-minato-kita 1-chome
Suminoe-ku, Osaka City, Osaka

(72) Inventor: Akane MIYAZAKI
20-20 Minami-hiradai, Miyamae-ku,
Kawasaki-shi, Kanagawa Prefecture

(72) Inventor: Kenji TAKESHITA
2-14-3 Minamitsukushino, Machida-shi,
Tokyo

(72) Inventor: Keiichi AKISHIKA
2-10-3 Tsukushino, Machida-shi, Tokyo

(72) Inventor: Yoshio NAKANO
2-46-44 Hirozawa, Hamamatsu-shi,
Shizuoka Prefecture

(74) Agent: Einosuke KISHIMOTO
Patent Attorney (and 4 others)

(54) [Title of the Invention] Method for Manufacturing Metallic Microparticles and Methods for Supporting Same Microparticles on Porous Carrier

(57) [Summary]

[Object] A method is provided that applies to a variety of metals and enables microparticles to be manufactured from metals or metal oxides stably and inexpensively.

[Means of Achievement] A metallic salt is dissolved in a polyhydric alcohol, and the resulting solution is heated at a temperature of 100 to 250°C (and preferably 150 to 200°C) to yield metallic microparticles in the polyhydric alcohol. A metallic salt is dissolved in a polyhydric alcohol, the resulting solution is impregnated into a porous carrier, and the carrier is heated at a temperature of 100 to 250°C (and preferably 150 to 200°C), yielding metallic microparticles formed in the fine pores of the carrier. A metallic salt is dissolved in a polyhydric alcohol, a porous carrier is suspended in the resulting solution, and the resulting suspension is heated at a temperature of 100 to 250°C (and preferably 150 to 200°C), yielding metallic microparticles formed in the fine pores of the carrier.

[Claims]

[Claim 1] A method for manufacturing metallic microparticles characterized in that a metallic salt is dissolved in a polyhydric alcohol, and the resulting solution is heated at a temperature of 100 to 250°C, yielding metallic microparticles formed in the polyhydric alcohol.

[Claim 2] The method for manufacturing metallic microparticles according to Claim 1, wherein the concentration of metallic salt in the polyhydric alcohol is 0.1 to 20 mmol/L.

[Claim 3] The method for manufacturing metallic microparticles according to Claim 1 or 2, wherein once the metallic microparticles have been formed in the polyhydric alcohol, a pH adjustor is added to adjust the pH of the solution to two or less, or to seven or more, and thereby prevent the metallic microparticles from aggregating.

[Claim 4] The method for manufacturing metallic microparticles according to Claims 1 through 3, wherein ethylene glycol, propylene glycol, polyethylene glycol, polypropylene glycol, or a mixture comprising two or more of these compounds is used as the polyhydric alcohol.

[Claim 5] The method for manufacturing metallic microparticles according to Claims 1 through 4, wherein the metal of the metallic salt is at least one transition/noble metal.

[Claim 6] The method for manufacturing metallic microparticles according to Claims 1 through 4, wherein the metal of the metallic salt is at least one transition/base metal.

[Claim 7] The method for manufacturing metallic microparticles according to Claims 1 through 4, wherein the metal of the metallic salt is at least one metal from Group Ib of the periodic table that has good electrical conductivity.

[Claim 8] The method for manufacturing metallic microparticles according to Claims 1 through 7, wherein a metal chloride, an oxide, an organic acid salt, an ammonium complex, or a mixture comprising two or more of these compounds is used as the metallic salt.

[Claim 9] The method for manufacturing metallic microparticles according to Claims 1 through 8, wherein a plurality of types of metallic salts are simultaneously dissolved in the polyhydric alcohol, and heated to yield composite metallic microparticles.

[Claim 10] A method for supporting metallic microparticles on a porous carrier, characterized in that a metallic salt is dissolved in a polyhydric alcohol, the resulting solution is impregnated into a porous carrier, and the carrier is heated at a temperature of 100 to 250°C, yielding metallic microparticles formed in the fine pores of the carrier.

[Claim 11] A method for supporting metallic microparticles on a porous carrier, characterized in that a metallic salt is dissolved in a polyhydric alcohol, a porous carrier is suspended in the resulting solution, and the resulting suspension is heated at a temperature of 100 to 250°C, yielding metallic microparticles formed in the fine pores of the carrier.

[Claim 12] The method for supporting metallic microparticles on a porous carrier according to Claim 10, wherein the concentration of metallic salt in the polyhydric alcohol is 10 to 200 mmol/L.

[Claim 13] The method for supporting metallic microparticles on a porous carrier according to Claims 10 through 12, wherein once these metallic microparticles have been formed in the fine pores of the carrier, the porous carrier that supports the metallic microparticles is immersed in an aggregation-preventing solution having a pH of two or less or of seven or more to prevent the metallic microparticles from aggregating, and is subsequently dried.

[Claim 14] The method for supporting metallic microparticles on a porous carrier according to Claims 10 through 13, wherein an acidic oxide, basic oxide, neutral solid, complex oxide, or a mixture comprising two or more of these compounds is used as the porous carrier.

[Claim 15] The method for supporting metallic microparticles on a porous carrier according to Claims 10 through 14, wherein ethylene glycol, propylene glycol, polyethylene glycol,

polypropylene glycol, or a mixture comprising two or more of these compounds is used as the polyhydric alcohol.

[Claim 16] The method for supporting metallic microparticles on a porous carrier according to Claims 10 through 15, wherein the metal of the metallic salt is at least one transition/noble metal.

[Claim 17] The method for supporting metallic microparticles on a porous carrier according to Claims 10 through 15, wherein the metal of the metallic salt is at least one transition/base metal.

[Claim 18] The method for supporting metallic microparticles on a porous carrier according to Claims 10 through 15, wherein the metal of the metallic salt is at least one metal that has good electrical conductivity.

[Claim 19] The method for supporting metallic microparticles on a porous carrier according to Claims 10 through 18, wherein a metal chloride, an oxide, an organic acid salt, an ammonium complex, or a mixture comprising two or more of these compounds is used as the metallic salt.

[Claim 20] The method for supporting metallic microparticles on a porous carrier according to Claims 10 through 19, wherein a plurality of types of metallic salts are simultaneously dissolved in the polyhydric alcohol, and heated to yield composite metallic microparticles.

[Claim 21] The method for supporting metallic microparticles on a porous carrier according to Claims 10 through 19, wherein the porous carrier is a fine pulverized body, with the fine pulverized body being held in a matrix between the fibers of a fibrous preform.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention] This invention relates to a method for reducing metal ions in a polyhydric alcohol to obtain highly dispersed metallic microparticles, and to a method for supporting highly dispersed and non-aggregating metallic microparticles on a porous carrier.

[0002] Stable metallic microparticles that are highly dispersed as described above are essential raw materials in catalysts, adsorbents, and absorbents comprising microparticulate metals or metallic oxides that are supported on the surfaces of porous supports in a dispersed state; functional glass comprising microparticulate metals or metallic oxides that are supported on vitreous substances in a dispersed state; coatings (especially functional coatings) comprising microparticulate metals or metallic oxides that are supported on oils, fats, or resins in a dispersed

state; functional films (especially magnetic storage media) comprising microparticulate metals or metallic oxides that have been affixed to tape-like plastic films; and in other applications.

[0003]

[Prior Art and Problems to Be Solved] Methods known for manufacturing microparticulate metals or metallic oxides (e.g., aerosol methods, CVD, and ALE) involve the heat-induced evaporation of metallic compounds having a relatively high vapor pressure, and modifying the resulting material into compounds having a low vapor pressure in a gas phase or in a state where the vapor is adsorbed onto the surface of a solid.

[0004] Nevertheless, such methods are limited by the types of metals that may be used, and are unsuited to industrial mass production due to the manufacturing costs necessitated by the specialized equipment employed in the actual manufacture thereof.

[0005] Furthermore, even when such methods are used, particles having a particle size of 10 nm or less are not readily obtained thereby.

[0006] The sol-gel method, which involves subjecting a metal alcoholate to hydrolysis, is another known method for manufacturing metallic microparticles; however, manufacturing costs are similarly high, and stable microparticles having a size of several nanometers prove difficult to obtain.

[0007] The reason for the difficulties so encountered in obtaining stable microparticles is believed to be due to the particles having chemically active surfaces, and inevitably tending to aggregate.

[0008] Moreover, there is no technique known for supporting microparticles having a size of several nanometers on solid surfaces stably and in high densities.

[0009] Given the foregoing circumstances, the issues cited hereunder must be resolved in order to obtain stable microparticulate metals or metallic oxides, and to support these metals or oxides on solid surfaces stably and in high densities:

[0010] • Obtaining fine first-order particles using a straightforward method

• Preventing the resulting first-order particles from aggregating

• Supporting the resulting microparticles in the fine pores of a porous carrier

[0011] The present invention has been designed to resolve the aforementioned issues, with an object thereof being to provide a method that applies to a variety of metals and enables microparticles to be manufactured from metals or metal oxides stably and inexpensively.

[0012] It is a further object of the present invention to provide a method with which these microparticles may be supported on a porous carrier stably and in high densities.

[0013]

[Means for Solving the Problems] The method for manufacturing metallic microparticles using the present invention shall first be described hereunder. The method for manufacturing metallic microparticles according to the present invention is characterized in that a metallic salt is dissolved in a polyhydric alcohol, and the resulting solution is heated at a temperature of 100 to 250°C (and preferably 150 to 200°C), yielding metallic microparticles formed in the polyhydric alcohol.

[0014] According to this method, the heating of the solution consisting of the metallic salt in the polyhydric alcohol causes the dissolved metal to react with the polyhydric alcohol, which is the solvent, and thereby enables insoluble, reduced metallic microparticles to be produced in the polyhydric alcohol.

[0015] The polyhydric alcohol used in the method for manufacturing metallic microparticles according to the present invention is an organic compound that has a plurality of alcoholic hydroxyl groups (–OH) in the carbon chains, with specific examples thereof including ethylene glycol, propylene glycol, polyethylene glycol, and polypropylene glycol. These compounds may be used singly or in combinations of two or more. Any polyhydric alcohol may be employed in the present invention, provided that metals may be dissolved thereby.

[0016] Polyhydric alcohols tend to form a type of hydrogen bond with the resulting metallic microparticles, and the protective-coating effect prevents the resulting first-order particles from coalescing, thereby enabling relatively stable microparticles having a diameter of ten nanometers or less to be obtained. In addition, polyhydric alcohols have relatively high viscosity near room temperature, which further prevents such particles from coalescing.

[0017] The reducing effect of the metal as caused by the polyhydric alcohol does not require the presence of a catalyst, and readily occurs merely from heating at temperatures of 100 to 250°C. The possibility that foreign substances will contaminate the resulting microparticles is accordingly eliminated.

[0018] Any metallic salt may be used as a raw material of the metallic microparticles, provided that it has the ability to dissolve in the polyhydric alcohol. Metallic salts that may be used should

reduce to metals by means of polyhydric alcohol reduction, with specific examples including salts of metals that exhibit good electrical conductivity, such as Pt, Pd, Rh, Ru, Ir, and other transition/noble metals; Fe, Ni, Co, and other transition/base metals; and Cu, Ag, Au, and other metals from Group Ib of the periodic table of the elements. The salts may be used singly or in combinations of two or more. Examples of the forms in which the salts may exist include metal halides, oxides, nitrates, organic acid salts, or complexed compounds such as ammonium complexes.

[0019] The concentration of metallic salts dissolved in the polyhydric alcohol is determined according to such criteria as the type of metallic salt and polyhydric alcohol. The yield of metallic particles per reactor volume will generally improve at higher concentrations; however, there is a high possibility that the microparticles will aggregate, and difficulties will be encountered in obtaining metallic microparticles with a particle size of five nanometers or less, as well as in obtaining stable colloidal solutions containing these microparticles. If the metallic salt concentration is 20 mmol/L or less, dramatic aggregation will not occur, and difficulties will be encountered in obtaining metallic microparticles with a particle size of five nanometers or less. Consequently, the concentration of metallic salt in the polyhydric alcohol is preferably 0.1 to 20 mmol/L, and more preferably 0.5 to 10 mmol/L.

[0020] In the method used in the present invention for manufacturing metallic microparticles, a plurality of types of metallic salts are simultaneously dissolved in the polyhydric alcohol, which enables microparticles ranging from alloys to composite metals to be formed in the polyhydric alcohol according to the composition of the plurality of metallic salts. This phenomenon indicates that the high activity of the atomic metals formed as result of the polyhydric alcohol reduction will cause them to bond randomly with the surrounding metallic microparticles should collisions occur therebetween (the bonding is of the atomic type, and is therefore as significant as a reaction). The resulting alloyed particles will not be subject to metallographic constraints (e.g., mutual solubility of molten metals), and the composition will be unambiguously determined according to the composition of the solution mixture and the reduction conditions. If the mixed microparticles are oxidized under optimal conditions, complex oxide microparticles will be obtained without being confined to the phase diagram.

[0021] After the metallic microparticles have been produced, a pH regulator is added to the polyhydric alcohol that contains the particles to adjust the pH of the solution to preferably two or

less, or seven or more, and more preferably to nine or more, thereby preventing the metallic microparticles from aggregating, and enabling a stable colloidal solution to be manufactured. Consequently, by adjusting the polyhydric alcohol that contains the resulting metallic microparticles to a pH of two or less, or seven or more, the surfaces of the metallic microparticles will become highly conductive, and the repulsive force thereby generated between the particles will prevent them from aggregating, or the like. The polyhydric alcohol that contains these metallic microparticles may accordingly be stored as a stable colloidal solution for long periods of time. Such colloidal solutions are easy to handle, and if an oil-based colloid is used, the colloidal solution will require no further modification to be able to mix with a variety of oils, fats, and resins. These solutions are therefore ideally employed in the manufacture of such articles as coatings (especially functional coatings) comprising microparticulate metals or metallic oxides that are supported in oils, fats, or resins in a dispersed state; and functional films (especially magnetic storage media) comprising microparticulate metals or metallic oxides that have been affixed to tape-like plastic films.

[0022] The methods used in the present invention to support the metallic microparticles on a porous carrier shall now be described hereunder.

[0023] A first method used in the present invention for supporting metallic microparticles on a porous carrier is characterized in that a metallic salt is dissolved in a polyhydric alcohol, the resulting solution is impregnated into a porous carrier, and the carrier is heated at a temperature of 100 to 250°C (and preferably 150 to 200°C), yielding metallic microparticles formed in the fine pores of the carrier.

[0024] A second method used in the present invention for supporting metallic microparticles on a porous carrier is characterized in that a metallic salt is dissolved in a polyhydric alcohol, a porous carrier is suspended in the resulting solution, and the resulting suspension is heated at a temperature of 100 to 250°C (and preferably 150 to 200°C), yielding metallic microparticles formed in the fine pores of the carrier.

[0025] The methods used in the present invention for supporting metallic microparticles on porous carriers enable the resulting metallic microparticles to be retained on the surface of porous inorganic oxide carriers at specific sites; e.g., solid acid sites and basic sites. The microparticles retained on the solid surface will remain in a high state of dispersiveness without aggregating, even if dried without any further modifications.

[0026] The supporting methods used in the present invention may be applied in the manufacture of such articles as catalysts, adsorbents, and absorbents comprising microparticulate metals or metallic oxides supported on the surface of a porous support in a dispersed state; and functional glass composed of microparticulate metals or metallic oxides supported on vitreous substances in a dispersed state. Carriers for metallic microparticles having a particle size of 50 nm or less have been difficult to obtain using conventional supporting methods that employ impregnation, adsorption, or the like; however, carriers for metallic microparticles having a particle size of five nanometers or less, and an average particle size of two to three nanometers, may be obtained with the supporting methods used in the present invention. Consequently, the surface area per weight of carrier, which is believed to be a factor that determines activity (e.g., catalytic activity), will be at least 30 times as great as encountered in conventional articles, and at least 1,000 times as great in the interface between the carrier and the supported substance, thereby enabling high activity to be obtained from a small amount of supported substance. This is especially advantageous in the preparation of catalysts in which expensive noble metals are supported.

[0027] The metallic microparticles produced in the fine pores of the porous carrier are captured and deposited on the carrier surface at the time by which their size has increased to approximately several nanometers, reducing the likelihood of coalescence due to thermal motion or the like. Consequently, microparticles having a size of approximately five nanometers or less will be obtained with the supporting methods of the present invention, even if a high concentration of metallic salt is dissolved in the polyhydric alcohol. The concentration of metallic salt in the polyhydric alcohol is preferably 10 to 200 mmol/L, and more preferably 20 to 100 mmol/L.

[0028] Once the metallic microparticles have been formed in the fine pores of the carrier by means of the supporting methods used in the present invention, it is desirable for the porous carrier on which the metallic microparticles are supported to be dried after being immersed in an aggregation-preventing solution having a pH of preferably two or less, or of seven or more, and more preferably of nine or more, to prevent the metallic microparticles from aggregating.

[0029] Examples of porous carriers include alumina, titania, silica, and other acidic oxides; magnesia, ceria, calcium carbonate, and other acidic/basic oxides; activated carbon, porous glass, and other neutral solids; and Al-Si, Al-Zr, Al-Ce, Ti-Si, Ti-Zr, Ti-Mn, and other complex oxides.

Although porous carriers are suitably selected according to the type of carrier metal when intended for such applications as catalysts, adsorbents, absorbents, and functional glass, the polyhydric alcohol solution in which the metallic salt is dissolved should, as a rule, be any variety that is able to penetrate into the fine pores.

[0030] The porous carrier may assume the form of a fine powder, and the carrier powder may be held in the matrix between the fibers of a fibrous preform.

[0031] The polyhydric alcohol and metallic salt employed in the supporting methods of the present invention should be identical to those employed in the method used in the present invention to manufacture metallic microparticles.

[0032] In the methods used in the present invention for supporting metallic microparticles on a porous carrier, a plurality of types of metallic salts are simultaneously dissolved in the polyhydric alcohol, which enables microparticles that range from alloys to composite metals to be formed according to the composition of the metallic salts. This phenomenon was described in the section relating to the method for manufacturing metallic microparticles.

[0033] The polyhydric alcohol solutions obtained after the metallic microparticles have been manufactured and supported on a porous carrier in accordance with the present invention will contain anions corresponding to the dissolved metallic compounds, as well as trace quantities of water, aldehydes, organic acids, and other reaction products. These products may be readily separated out and removed from the polyhydric alcohol by means of distillation or the like, thereby enabling the polyhydric alcohol to be recovered and reused.

[0034]

[Embodiments of the Invention] The present invention shall be described in detail below with reference to working examples.

[0035] Working Example 1

(1) Reduction of Ru^{3+} with ethylene glycol

78.5 mg of ruthenium (III) chloride trihydrate was dissolved in one liter of ethylene glycol to prepare a 0.3 mmol/L solution. The solution was introduced into a glass reactor fitted with a reflux condenser, and heated under stirring for 0.5 hrs in a 180°C oil bath in an N_2 gas stream.

[0036] The reactor was subsequently quenched in an ice-cold water bath to yield "Solution A," which contained a solid component (microparticles). The microparticles were obtained by filtering Solution A.

[0037] The resulting microparticles were dried and then identified by means of X-ray diffractometry (XRD). The X-ray diffraction pattern is shown in FIG. 1. The resulting microparticles were able to be identified as Ru metal in the form of perfectly hexagonal crystals.

[0038] The microparticles were also observed using a transmission electron microscope (TEM), which revealed that the first-order particles with a particle size of five nanometers or less formed into aggregates of up to approximately 50 nm. The electron photomicrograph thereof is shown in FIG. 2.

[0039] The filtrate obtained once the microparticles had been removed was analyzed using an argon plasma emission spectrometer (ICP). No Ru residues were revealed.

[0040] (2) Preventing aggregation

The pH of Solution A that had been obtained by the same procedure as in Working Example 1 was measured and found to be approximately three. The zeta potential of the microparticles in Solution A was measured using a laser Doppler electrophoresis device and found to be +25 mV.

[0041] An aqueous solution of 0.1 N hydrochloric acid or ammonia was added dropwise into Solution A to vary the pH over a range of 1 to 10, and the change in the zeta potential was measured. The results are shown in FIG. 3.

[0042] The absolute value of the zeta potential was found to rise sharply when the pH was two or less, or seven or more, and especially nine or more. These results reveal that if the pH is adjusted to two or less, or seven or more, and especially nine or more, the amount of electrostatic charge of the metallic first-order microparticles will increase, and the electrostatic repulsive charge will be able to prevent the first-order microparticles from aggregating.

[0043] (3) Preparation of metallic colloid

0.1 N ammonia water was added dropwise into Solution A to adjust the pH to 10, after which the solution was left to stand for ten hours at room temperature under vigorous stirring. The resulting metallic colloid solution was designated as "Solution B."

[0044] Solution B showed no evidence of sedimentation even when left to stand for one week after stirring had been stopped. A solvent was vapor-deposited onto a glass plate, and the

resulting microparticles were observed using transmission electron microscopy, which revealed that second-order particles (10 to 20 nm in size) had formed.

[0045] Working Example 2

(1) Supporting microparticles on porous carriers

4.42 g ruthenium chloride (III) trihydrate was dissolved in one liter of ethylene glycol to prepare a 16.9 mmol/L solution. The solution was introduced together with 20 g granular γ-alumina (60 mesh or less) into a glass reactor fitted with a reflux condenser, and heated under stirring for one hour in a 180°C oil bath while being passed through N_2 gas.

[0046] A 0.3 mol/L $NaNO_3$ aqueous solution was added to the resulting suspension in an amount that was nine times as great in terms of the volume thereof, whereupon suction filtration was performed. The solid component was dried under reduced pressure at 120°C, and any ethylene glycol that had adhered thereto was removed.

[0047] The solid component was analyzed with an X-ray fluorescence spectrometer (Mo • XFS), which confirmed the presence of Al and Ru. The resulting XFS spectrum is shown in FIG. 4.

[0048] The results obtained from TEM observation of the solid component demonstrated that the Ru was supported on the alumina in the form of dispersed particles that were approximately five nanometers or less. The TEM microphotograph is shown in FIG. 5.

[0049] The solid component was also subjected to hydrogen reduction for three hours at 400°C, and the particle sizes of the supported Ru were then measured by H_2 and CO adsorption. The resulting values were respectively 2.4 and 2.7 nm, which coincided well with the results obtained from TEM microscopy.

[0050] The filtrate was analyzed using ICP, which revealed that 0.077 mmol/L (ethylene glycol) was detected as Ru residue, and 99.5% of the dissolved amount was supported on the alumina.

[0051] (2) Supporting microparticles on various carriers

The capacity for microparticles to be supported on a variety of porous carriers was measured in the same manner as in (1) with the exception that the granulated γ-alumina porous carrier was substituted with SiO_2, MgO, and Al_2O_3, and various concentrations of dissolved ruthenium chloride were used. The results are displayed in Table 1.

[0052]

[Table 1]

Porous carrier	Concentration of dissolved Ru (mmol/L)	Concentration of filtered Ru (mmol/L)	Size of supported Ru particles (nm)
SiO_2	0.177	0.047	5.2
MgO	0.141	0.009	4.8
Al_2O_3	0.141	0.000	2.5

Concentration: mmol/L (ethylene glycol)
Particle size: nm (measured by H_2 adsorption)

[0053] (3) Supporting various metals

A variety of microparticles were formed using the same procedure employed in (1), with the exception that the ruthenium chloride was substituted with Fe chloride, Pt chloride, and Au chloride, and that the dissolved metals were used in varied concentrations. The sizes of the resulting metallic microparticles were observed with TEM microscopy. The results are displayed in Table 2.

[0054]

[Table 2]

Metallic salt	Concentration of dissolved metal (mmol/L)	Size of resulting microparticles (nm)
Fe chloride	0.25	5 or less
Pt chloride	0.31	5 or less
Au chloride	0.14	5 or less

Concentration: mmol/L (ethylene glycol)
Particle size: nm (measured by H_2 adsorption)

[0055]

[Effect of the Invention] The method used in the present invention for manufacturing metallic microparticles applies to a variety of metals and enables microparticles to be manufactured from metals or metal oxides stably and inexpensively.

[0056] Furthermore, the methods used in the present invention for supporting metallic microparticles on porous carriers enable the same microparticles to be supported on porous carriers stably and in high densities.

[Brief Description of the Drawings]

[Figure 1] Graph depicting an X-ray diffraction pattern of microparticles. The vertical axis in the graph indicates the diffraction pattern position of metallic ruthenium.

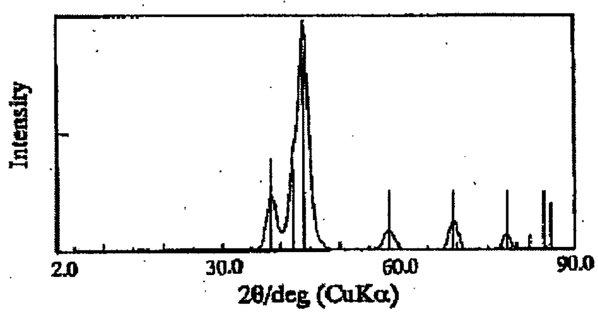
[Figure 2] Photomicrograph of microparticles observed with TEM microscopy.

[Figure 3] Graph showing the relationship between pH and zeta potential.

[Figure 4] X-ray fluorescence spectrum of solids.

[Figure 5] Photomicrograph of solids obtained by TEM microscopy.

[Figure 1]



[Figure 2]

Photograph in lieu of drawing

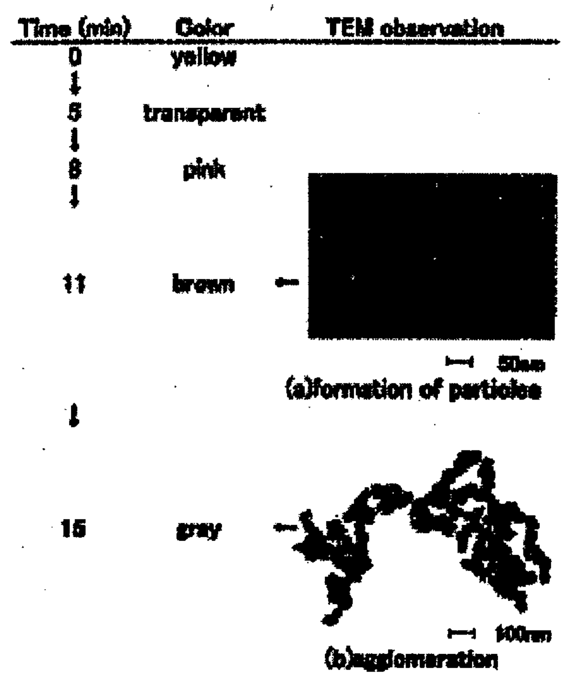
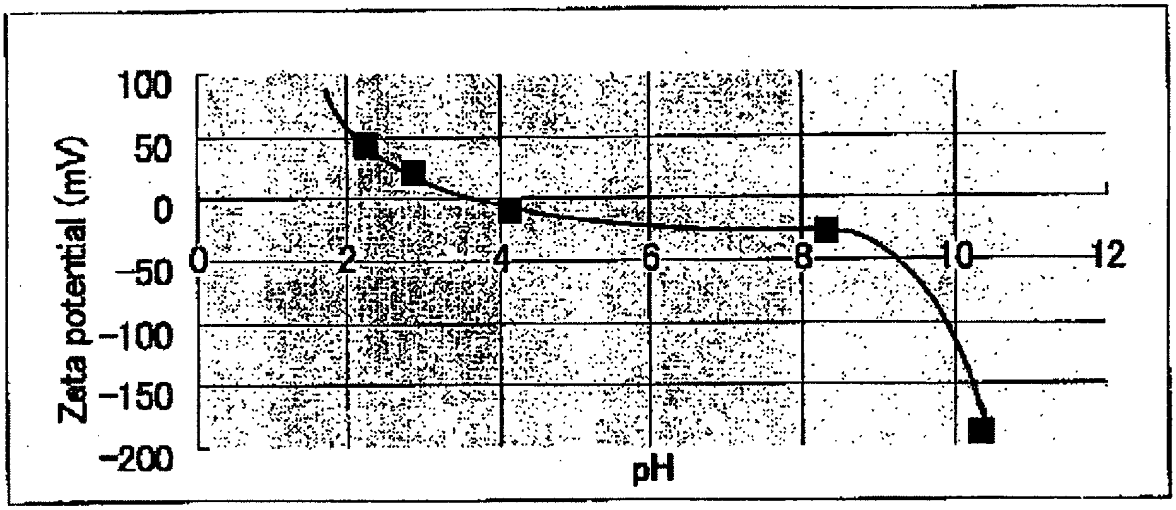


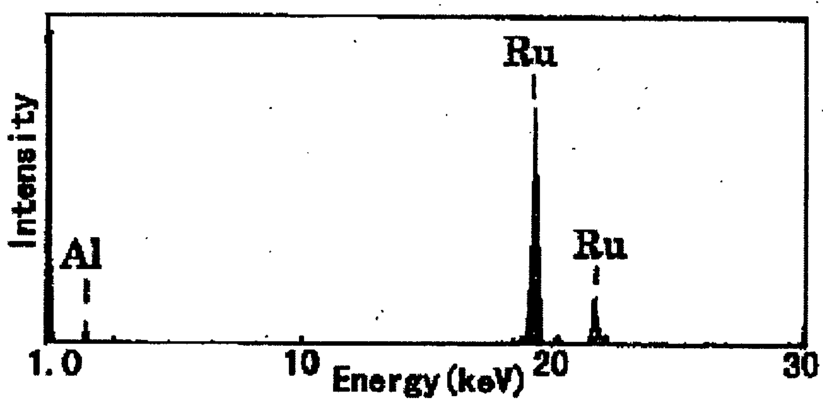
Figure 1. Schematic time course of the reaction and TEM observation of the solution.

[Figure 3]

Relation between the pH of colloidal solution and ζ potential



[Figure 4]



[Figure 5]
Photograph in lieu of drawing